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Abstract

Management of plant residues plays an important role in maintaining soil quality and nutrient availability for plants and microbes. However, there is considerable uncertainty regarding the factors controlling residue decomposition and their effects on greenhouse gas (GHG) emissions from the soil. This uncertainty is created both by the complexity of the processes involved and limitations in the methodologies commonly used to quantify GHG emissions. We therefore investigated the addition of two soil residues (durum wheat and faba bean) with similar C:N ratios but contrasting fibres, lignin and cellulose contents on nutrient dynamics and GHG emission from two contrasting soils: a low-soil organic carbon (SOC), high pH clay soil (Chromic Haploxerert) and a high-SOC, low pH sandy-loam soil (Eutric Cambisol). In addition, we compared the effectiveness of the use of an Infrared Gas Analyzer (IRGA) and Photoacoustic Gas Analyser (PGA) to measure GHG emissions with more conventional gas chromatography (GC). There was a strong correlation between the different measurement techniques which strengthens the case for the use of continuous measurements approaches involving IRGA and PGA analyses in studies of this type. The unamended Cambisol released 286% more CO_2 and 30% more N_2O than the Haploxerert. Addition of plant residues increased CO_2 emissions more in the Haploxerert than Cambisol and N_2O emission more in the Cambisol than in the Haploxerert. This may have been a consequence of the high N stabilization efficiency of the Haploxerert resulting from its high pH and the effect of the clay on mineralization of native organic matter. These results have implications management of plant residues in different soil types.

Key words: crop residues**,** carbon dioxide, greenhouse gas, nitrous oxide, residue decomposition

Introduction

Agriculture forestry and related land uses are responsible for just under 25% of global greenhouse gas emissions (IPCC 2014). Agronomic practices are recognized as key opportunities to reduce GHG emissions (particularly for N_2O and CO_2). The addition of plant residues to the soil from crops and cover crops is of significant importance to crop management strategies to enhance soil organic C (SOC) and soil fertility, and to offset agricultural GHG emissions (Lugato et al. 2014). However, decomposition of residues will also add nitrogen (N) to the soil, and with the default N_2O Emission Factor of 1% of the added N in the IPCC (2006) methodology, a proportional increase in estimated N_2O emissions is predicted. However, IPCC predictions have been developed around limited experimental data and recent studies indicate that default Emission Factors may overestimate residues N_2O emissions (Jeuffroy et al. 2013). GHG emission after crop residue amendment is related to both its decomposition and the microbial activity of soil and depends from several factors linked to the environment, soil proprieties and crop residue traits (Aulakh et al. 1991; Powlson et al. 2011). In particular, the GHG emission from the soil are mediated by soil porosity (Killham et al. 1993), pH (Mörkved et al. 2006), organic C and N content (Hayakawa et al. 2009), microbial community (Graf et al. 2016), texture (Chen et al. 2013), soil temperature (Kesik et al. 2006), and moisture content, all of which regulate gas production processes and emission (Skiba and Ball 2002; Rees et al. 2013). Moreover, crop residue addition to the soil can also

indirectly affect GHG emissions, providing a source of readily available C and N in the soil, stimulating microbial activity (Aulakh et al. 2001; Huang et al. 2004), promoting the decomposition of native soil organic carbon, and altering soil aeration, water holding capacity, oxidation and denitrification processes in the soil (Fontaine et al. 2004; Derrien et al. 2014).

With regard to the crop residue characteristics, the most important property is its C:N ratio that determines organic N dynamics in the soil (Heal et al. 1997; Baggs et al. 2003; Al-Kaisi and Yin 2005; Garcia-Ruiz and Baggs 2007). In particular, it has been shown that higher N_2O emissions occur from soil after the incorporation of residues with low C:N ratio, such as legumes, rather than after cereal straw as a result of mineralization processes (Baggs et al. 2000; Huang et al. 2004; Raiesi 2006). On the contrary, low N_2O emissions were reported following the application of crop residues with high C:N ratios (Gentile et al. 2008). However, it has also been shown that the incorporation of crop residues with high C:N ratios may provide the energy for the denitrification process, and this can increase N_2O emissions (Sarkodie-Addo et al. 2003). Other crop residue properties can play an important role on the decomposition process influencing microbial activity, including lignin (Palm and Rowland 1997), lignin:N ratios (Curtin et al. 1998) polyphenol (Muhammad et al. 2010), water soluble phenolic contents (Palm and Rowland 1997), percentages of soluble C and N (Cogle et al. 1989), neutral detergent fiber (NDF). This understanding of the multiple drivers responsible for GHG emissions from crop residues is helpful in interpreting research findings. Baggs et al. (2000) found an increase of N_2O emissions after lettuce incorporation into the soil due to its low C:N ratio. However, Tanveer et al. (2014) and Zou et al. (2004) observed a reduction of N_2O emission after incorporation of low C:N crop residue of corn and rice straw. This apparent contradiction may be a consequence of the interaction of multiple factors controlling emission. Shan and Yan (2013), in a meta-analysis, reported that the application of canola, bean and lettuce residues increased N_2O emissions more than with other kind of crop residues. With regard to CO_2 emissions Muhammad et al. (2010) observed higher emissions in soil amended with alfalfa than with sugarcane, maize, sorghum and cotton and attributed such result to a release of more easily degradable and soluble C in alfalfa than with other crop residues. Chen et al. (2015) observed a general increase of CO_2 emissions from a soil amended with different types of residues but with higher cumulative emissions in peanuts, soybean and maize than in other cereals due to their higher N and lower neutral detergent fiber (NDF) content.

An accurate quantification of CO_2 and N_2O emission following return of crop residues to soils is required to develop efficient strategies to reduce the environmental impact of farming practices. Presently, static chamber methods coupled with gas chromatography (GC) analysis are the most widely technique used to quantify GHG losses in field and laboratory experiments. However, the method is time consuming and entails a wide series of operations from the manual sampling to the laboratory analysis, introducing errors, and making difficult to implement high resolution monitoring over time (Tirol-Padre et al. 2014). In order to obtain high resolution temporal data, InfraRed Gas Analyzer (IRGA) and Photoacustic Gas Analyzer (PGA) has been used in agricultural GHG emissions studies (Luo and Zhou 2006; Lawrence et al. 2009; Stackhouse et al. 2011). IRGA allows to measure CO_2 fluxes using an infra-red sensor and PGA is a photo-acoustic infrared multi-gas monitoring system that allows to measure simultaneously CO_2, N_2O and CH_4. Measurement of CO_2 efflux by IRGA systems are usually based on different methodology proposed by the manufacturing companies and there isn't an internationally recognized protocol creating

uncertainties in the comparison between different instruments (Mills et al. 2011). PGA has been widely used in field experiments and several authors found a high correlation between CO_2 and N_2O measurements made with PGA and GC (Klein et al. 2008; Iqbal et al. 2013). Other authors reported an overestimation of emission on the data obtained with PGA than GC (Yamulki and Jarvis 1999). Furthermore, the precision of measurement may also depend from the soil type and soil cover, which can affect the assessment of emission spatial variability. The precision of the various instruments (IRGA and PGA comparing to the widely used CG) in measuring GHGs emission has never been measured. However, in contrast to the GC-based methodology, these systems are able to provide a continuous measurement of the GHGs emission, thus allowing to better study the trend of the emission from the soil and its relationship with agronomical management techniques and environmental variability. In addition, IRGA and PGA has not been previously directly compared.

Soil GHG emissions from Cambisols which occur widely in cool temperate climates have widely studied in the past whereas the effect of soil characteristics typical of the Mediterranean such as vertisols, with their high clay content high pH and low organic carbon content, on crop residue decomposition and gaseous emissions are less known. The aims of the present study were: (i) to evaluate the short-term emissions of N_2O and CO_2 after the addiction of two crop residues with different structural fibre composition (either faba bean and wheat), in two soils with contrasting proprieties, a Chromic Haploxerert with a high clay content and a Eutric Cambisol with a sandy-loam texture; (ii) asses the flexibility of two systems for the high temporal resolution measurements (IRGA and PGA), to measure soil GHG emissions from soils with different emission levels in controlled conditions. Experiments were undertaken in a controlled pot setup over a short period and in the absence of plants in order to simulate the effects of crop residues between cropping cycles. These conditions avoided strong time-related variation in the emission due to the impoverishment of the ready available N pool and living plant C inputs to and mineral uptake from soil, which could have altered the emission rates.

Materials and Methods

An experiment was established during 2014 in controlled environment conditions at Scotland's Rural College (SRUC) Edinburgh. A complete randomized factorial design with three replicates was adopted. Treatments were soil: Eutric Cambisol and Chromic Haploxerert (Vertisol); and kind of plant residue added: faba bean residue, durum wheat residue or unamended control. The Cambisol was collected at nine locations per plot from the top 20 cm at Bush Estate (lat, 55° 51' N, long, 3° 12' W; 199 m a.s.l.) near Edinburgh (Scotland), the Haploxerert (Vertisol) was collected at the Pietranera Farm (37°30' N, 13°31 E; 178 m a.s.l.) in Santo Stefano Quisquina (Sicily). Both soils were sampled in early October 2014. Soil was collected from conventional tilled experimental plots at the Bush Estate in Scotland and from conventionally tilled plots at Pietranera farm in Sicily (Table 1). At both sites the soil was collected in plots previously cultivated with cereals (wheat in Sicily and barley in Scotland). Further information regarding the soil sampling sites are available in Vinten et al. (1992) and Amato et al. (2013), respectively. Before establishing the experiment, soil was air-dried and passed through a 2 mm mesh and visible roots and organic residues were removed, and then mixed thoroughly before use; water hold capacity of both soils were measured on a weight basis. Oven-dried crop biomass of wheat (cv. Simeto) and faba bean (cv. Gemini) (see

Table 2 residues traits), cultivated at Pietranera farm, were ground to pass a 1 mm screen, mixed, and used as crop residues.

Pots were 10 cm in diameter and 25 cm heigh, and were filled with 1.5 kg of soil to achieve a bulk density of 1.25 g cm^{-3}. Crop residues were mixed with the soil at a rate of 5 g crop residue per kg of soil. The bottom part of the pot (15-25cm depth) was filled with sand. Then, pots were brought to 60-70% of the water holding capacity. After each sampling an amount of water corresponding to the evaporation losses was added to each pot and the pots were randomized inside the greenhouse. During the experiment, soil temperature was recorded using a temperature data logger (EL-USB-3, Lascar Electronics, United Kingdom).

Both CO_2 and N_2O soil emissions were measured three time per week, on 22 sampling occasions, by means of two different methods: an online Infrared Gas Analyzer (IRGA, EGM-4 CO_2, PP system, USA) and a Photoacoustic Gas Analyser (PGA, INNOVA 1412, LumaSense Technologies A/S, USA). Measurements were always taken between the 9:00 and the 15:00 and each time the equipment order was reversed. The IRGA was equipped with a SRC-1 Soil Respiration Chamber equipped with a fan, with of 10 cm of diameter and 15 cm height, sealed on top of the pot by an airtight rubber. The air from the chamber was send to the analyser at flow rate of 0.1 l min^{-1}. After 15 seconds of flushing, the chamber was placed above the pot, equilibrated for 15 seconds, than the CO_2 concentration was measured every 5 seconds and the flux was calculated from the concentration increase over time until a good linear fit was obtained.

The PGA was equipped with a PVC chamber with a 10 cm of diameter and 10 cm height, connected to the equipment by two small rubber pipe on the chamber top, and sealed above the pot by a rubber seal. The analyser automatically pumped ~0.1 l min^{-1} of air from inside the chambers and performed the analysis with a 5-second sampling integration time and a fixed flushing time: 8 seconds for the chamber and 3 s for the tubing. The PGA instrument was calibrated in the lab for CO_2 and N_2O by the LumaSense technologies company, with a gas concentration of 3496.8 ppm for CO_2 and 51.32 ppm for N_2O, and it's detection limits were of 1.5 ppm for CO_2 and 0.03 ppm for N_2O. The equipment performed a built-in compensation for water and cross interferences. Before the flux measurements, the instrument analyzed ambient air for about 30 min until readings for CO_2 and N_2O were stable. The overall time for sampling and measurement of CO_2 and N_2O concentration and dew-point temperature was approximately 70 seconds; each measurement was made every two minutes.

Gas flux measurement (CO_2 from both IRGA and PGA, and N_2O from PGA), in two different periods during the experiment, were compared with analyses by gas chromatography in order to confirm the reliability of the instruments. CO_2 and N_2O emissions were measured using the static closed chamber technique (Hutchinson and Mosier 1981). A chamber of polyvinyl chloride (PVC), with 10 cm of diameter and 15 height and a lid with a gas sampling port was sealed above each pot for 60 min. Before and after this period gas samples were collected in portable evacuated glass vials (Chadwick et al. 2014), transported to the lab and analyzed by a gas chromatography (Agilent 7890a, Agilent Technologies Ltd, Stockport, UK) equipped with a thermal conductivity detector (TCD, detection limit for CO_2 of 23.9 ppm) and an electron capture detector (ECD, detection limit for N_2O of 0.074 ppm). Fluxes of CO_2 and N_2O were calculated from the increase in

concentration in the chamber corrected for the chamber air temperature using the following relation (Jantalia et al. 2008):

$$f = \frac{\Delta C}{\Delta t} \times \frac{V}{A} \times \frac{m}{Vm}$$

where $\Delta C/\Delta t$ is the gas increment during the chamber closure time, V is the volume of the chamber, A is the soil area, *m* is the molecular weight of the gases and *Vm* is the gas molar volume corrected for the ambient temperature.

The total amount of N_2O and CO_2 emissions were calculated by linear interpolation between consecutive using the following equation (Cai et al. 2012):

$$Cumulative\ emission\ of\ N_2O\ or\ CO_2 = \sum_{i=1}^{n} (F_i + F_{i+1})/2 \times (t_{i+1} - t_i) \times 24$$

where *F* are the emission flow of N_2O and CO_2 at the i^{th} measurement, (t_{i+1}-t_i) is the time length between two adiacent measurements and n is the total measurement number.

Plant dry matter (oven drying), ether extract (Method 920.39, diethyl ether, traditional Soxhlet extraction), total N (Kjeldahl) and crude protein (calculated from the total N by standard Jones factor, N x 6.25) were analyzed following methods described by AOAC (1995). Neutral detergent fibre (NDF), acid detergent fibre (ADF), acid detergent lignin (ADL), cellulose and hemicellulose where analysed following the sequential method proposed by Van Soest et al. (1991) and using a Fibertec System M 1020 extractor (Foss, Höganäs). The soluble fraction was obtained by boiling 1 g of ground residues in deionized water (100°C) for 30 min followed by extraction with a neutral detergent (EDTA and Na lauryl sulphate at 100°C) for 60 min to obtain the NDF fraction. ADF extraction was performed by boiling the sample for 60 minutes in an acid detergent solution (Cetyltrimethylammonium (CTAB) in H_2SO_4). Then, the residual detergent was removed by washing the sample with hot water. Finally, the ADF was then treated with 72% H_2SO_4 (w/w) for 3 hours at ambient temperature and the final mass of the non-extractable fraction was considered as lignin (ADL). Cellulose was calculated as the difference between ADF and ADL while hemicellulose ad the difference between NDF and ADF. Ash and ADL ash measurements were performed at 550°C for 4 h. For each residue type the analyses were performed in triplicate. Total C of biomasses and soils were analysed by an automated analyser (Flash 2000, Thermo-Finnigan, Glasgow, UK).

At the end of the experiment, two soil samples from each pot were collected: one from the top to 5 cm depth and the other from 5 to 15 cm depth. Soil pH was measured in a 1:5 (v/v) suspension of soil in water. Dissolved organic C (DOC) content in the soil was determined by a total organic C analyser (DC-80, Rosemount Analytical, Inc. Dohrmann Division, USA) after the removal of inorganic C by acidifying the sample. Concentrations of NH_4^+-N and NO_3^--N were determined from 10 g of soil extracted with 100 ml of 2M KCl (1:5 ratio); then the filtered extract NH_4^+-N and NO_3^--N concentrations were measured by a continuous flow analysis autoanalyser (SAN SYSTEM, Skalar Analytical B.V., Netherland).

Analysis of variance (ANOVA) was undertaken using a Mixed model according to the statistical design in SAS environment (SAS Institute 2008). Treatment means were separated using *p* differences of the LSMEANS.

Regressions between GC and IRGA, and GC and PGA, for CO_2, and for CO_2 and N_2O, respectively, were computed. Soil CO_2 emission rate measurements from IRGA and PGA were compared on the 22 sampling occasions. Comparisons were made by a regression analysis and the index of agreement (IoAd) (SAS Institute 2008; Bennett et al. 2013).

Results

The temperature inside the greenhouse during the experiment ranged from a minimum of 17°C to the maximum of 28.5°C, with an average of 20.5°C, while soil temperature ranged from a maximum of 27°C to a minimum of 20°C with a slight decreasing trend from the start to the end of the experiment (Fig. 1). The chemical composition of the plant residues used in the present study, expressed as percentages, are reported in Table 2. The N content of faba bean and durum wheat were comparable (1.4% vs 1.3%, respectively). With regards to the other constituents, marked differences were found between the plant residues. In particular, faba bean had higher ADF (+66 %), ADL (+186%), cellulose (+60 %), and NDF (+19%) than wheat, and a lower content of hemicellulose (–51 %) (Table 2).

Carbon and nitrogen dynamics

The Haploxerert used in the present study had a high pH (8.1) and high clay and low total C content (1.39%), whereas the Cambisol had a near neutral (6.6), low clay and high C content (2.48%). Interaction between soil and residue type for these soil properties by the end of the experiment was strong and significant ($p<0.05$) (Table 3). As expected, the addition of organic residues mostly increased DOC in both the top- and sub-soil layers of the Haploxerert (on average by 52.5% compared to unamended control), whereas there was no significant effect on the Cambisol.

The soil incubation, either with or without plant residues incorporation, decreased soil pH by 0.86 in the Cambisol and 0.33 in the Haploxerert. The effect of the addition of organic residues to the soil pH varied with both the soil and kind of biomass incorporated: in the Cambisol, addition of wheat residues significantly decreased pH in the top- and sub-layers when compared with the unamended control whereas addition of faba bean residues did not influence soil pH. In the Haploxerert, no effect of the addition of organic residues on soil pH were found in both soil layers.

The concentration of NH_4^+-N was higher in the Haploxerert than Cambisol, and this particularly apparent in the sub-layer. The role of the addition of organic residues on soil NH_4^+-N depended on the soil and kind of biomass added: addition of durum wheat residues increased soil ammonium-N in top-layer of both soils (+40% in the Cambisol and +102% in the Haploxerert), whereas NH_4^+-N in the soils amended with faba bean residues was similar to those of the controls. In the sub-layer of the Cambisol, the effect of the addition of the organic residues was similar to that observed in the top-layer, whereas addition of both residues strongly increased the NH_4^+-N of

263 Haploxerert comparing to the unamended control (+133% in faba bean and +454% in wheat
264 residues).

265 The concentration of NO_3^--N in both layers was significantly higher in the Cambisol when
266 compared with the Haploxerert and this occurred irrespective of the addition of organic residues. In
267 the Cambisol, addition of faba bean residues reduced NO_3^--N more than wheat residues, especially
268 in the sub-layer, when compared with the unamended control. In the Haploxerert, NO_3^--N in both
269 layers did not vary with the addition of plant residues.

270 NH_4^+-N:NO_3^--N ratio differed considerably in the different soil types: in the unamended
271 controls, it was 6.467 in the Haploxerert and 0.006 in the Cambisol. In the latter, addition of organic
272 residues to the soil did not influence the NH_4^+-N:NO_3^--N of either the top- or sub-layer. In the top-
273 layer of Haploxerert, the addition of organic residues reduced the NH_4^+-N:NO_3^--N ratio, especially
274 when faba bean residues were added. In the sub-layer, an opposite result was found and thus
275 addition of organic residues increased the NH_4^+-N:NO_3^--N ratio, especially when wheat residues
276 were added.

277 **Greenhouse gas emissions**

278 Carbon dioxide fluxes, measured with IRGA, ranged from a minimum value of 0.11 g m^{-2} h^{-1}
279 to a maximum value of 3.64 g m^{-2} h^{-1} (Fig. 2). For almost the entire experimental period, the
280 Cambisol had a higher CO_2 emission flux than the Haploxerert. At the beginning of the experiment
281 the two soil reached the maximum emission flux at the first and second day of measurement with
282 fluxes of 3.58 g m^{-2} h^{-1} for the Cambisol and 1.42 g m^{-2} h^{-1} for the Haploxerert.

283 The highest CO_2 fluxes were recorded in both soils amended with wheat straw whereas the
284 lowest in the unamended controls. The differences in emission between the two soils were strong in
285 the first two weeks of measurement, where the 53.8% and 46.2% of total CO_2 were emitted from
286 the Cambisol and the Haploxerert, respectively. After the first two weeks of measurement, the
287 differences between the two soils reduced and the emission decreased until the end of the
288 experimental period.

289 The CO_2 emissions measured with PGA showed a similar trend to those acquired by IRGA.
290 However, in the first part of the experimental period, PGA emissions were slightly higher than
291 those observed by the IRGA, especially from the Cambisol. In the second part of the experiment, no
292 differences between the techniques were found (Fig 2).

293 Total CO_2 emissions were 74% lower in the unamended Haploxerert (198 g CO_2 m^{-2})
294 compared to the Cambisol (765 g CO_2 m^{-2}). Addition of plant residues to the soil increased total
295 emission to a different extent depending on the soil under study (interaction Soil x Residue Type
296 significant $p<0.001$): in the Cambisol, addition of faba bean and wheat resulted in an increase of
297 24% and 88%, respectively, of the total CO_2 emissions. In the Haploxerert, no differences were
298 found between the kind of biomass incorporated, which, on average, increased total CO_2 emission
299 by 171% compared to the unamended control (Fig 4).

300 Emissions of N_2O during the experiment ranged from 0.022 to 0.348 mg m^{-2} h^{-1} (Fig 5).
301 However there were large differences between soils with emissions of 0.024 mg m^{-2} h^{-1} to 0.117 mg

m^{-2} h^{-1} and from 0.022 mg m^{-2} h^{-1} to 0.348 mg m^{-2} h^{-1} in the Haploxerert and Cambisol, respectively. The Cambisol reached a N_2O emission peak at 7 days after the beginning of the experiment, whereas the Haploxerert soil showed a continuous and constant reduction of the N_2O emission from the beginning of the experiment until the end of the trial. In addition, marked differences between amended and unamended soil were observed in Cambisol during the first half of experiment. The highest fluxes were measured in both soils amended with wheat straw. Cumulative N_2O emission in the unamended controls of the Cambisol soil was 30% higher than in Haploxerert soil (85.1 and 59.9 mg N_2O m^{-2}, respectively). Crop residue addition had a different effect in each soil (interaction Soil x Residue Type significant $p<0.001$). In the Cambisol, N_2O emissions in the pots amended with wheat was 159.8 mg N_2O m^{-2}, (+88% more than the control) and that of the pots amended with faba bean was 127.0 mg N_2O m^{-2}, (+49% than the control). In the Haploxerert, faba-bean added pots emitted in total 80.8 mg N_2O m^{-2} (+35% than the control) and that added with wheat 67.2 mg N_2O m^{-2} (+12% than the control; Fig 6).

Comparisons of gas measurement techniques

Few differences were found for the IRGA and PGA in CO_2 measurement when compared with that from the GC. The determination factor was 0.937 (y_{GC}=1.0534x_{IRGA}-0.0221 g $CO_2 m^{-2}\ h^{-1}$) and 0.925 (y_{GC}=0.9887x_{PGA}-0.0095 g $CO_2 m^{-2}\ h^{-1}$) for IRGA and PGA, respectively and index of agreement was 0.998 for both instruments.

With regards to the N_2O measurement, the linear regression between GC and PGA showed a relatively high relationship between the results (R^2=0.90; (y_{GC}=0.8993x_{PGA}-0.0063 mg $N_2O m^{-2}\ h^{-1}$)), although PGA-N_2O were, on average, 5.2 % higher than the GC-N_2O measurements. However, in this case, the index of agreement was also 0.998.

The comparison between CO_2 measurements obtained by IRGA and PGA across the entire experimental period (more than 600 measurements) showed a high correlation between the two instruments (R^2=0.95; IoAd=0.996; (y_{IRGA}=1.0118x_{PGA}-0.0003 g $CO_2 m^{-2}\ h^{-1}$). However, the cumulative CO_2 emissions measured by PGA were on average 9% higher than those measured by IRGA. Differences in CO_2 fluxes from the two soilwere apparent from the different measurement techniques. Thus although the overall CO_2 fluxes measured by PGA were 6% higher than IRGA, such differences were up to 10% greater when the conmparison was limited to the Haploxerert soil, and up to 17% when only the control plots were consdered. In the Cambisol the differences between the instruments were lower at around 5%.

Discussion

N_2O and CO_2 emission and soil properties

This study evaluated the effect of soil incorporation of two different plant residues on N_2O and CO_2 emissions. The characteristics of two soils were distinctly different, with the Cambisol having a low pH and high SOC while the Haploxerert had a high pH and low SOC. Emissions and soil parameters varied according to both the kind of residue added and the soil type. The total CO_2 and N_2O emissions, (measured by PGA), from the unamended Cambisol were 249% and 40% higher than the unamended Haploxerert, respectively, suggesting large differences in biochemical and microbial activity between both soils driven by differences in soil physical and chemical

properties. Moreover, the differences in CO_2 emissions between the two soils followed the differences in stable-C (TOC was 78% higher in the Cambisol than in Haploxerert) and readily available-C (DOC in the Cambisol was double that in the Haploxerert). This latter form, although it may be preferentially utilized by soil microorganisms, can be protected by soil aggregates or adsorbed by mineral particles (Majumder and Kuzyakov 2010; Steinbeiss et al. 2008; Shi et al. 2014). The higher CO_2 emissions (per unit of carbon present in the soil) from Cambisol were nevertheless a reflection of differences in the carbon pools. Such a differences suggest that the Haploxerert had a relatively low respiration rate, which may have been a consequence of protection by the higher clay content in the Haploxerert of SOC pools (Baldock and Skjemstad 2000; Krull et al. 2003; Lutzow et al. 2006; Alluvione et al. 2013; Six and Paustian 2014), and coupled with relatively low soil microbial activity due to a low free substrate availability. Another important aspect related to the clay content is its mineralogy; the Haploxerert is characterized by prominent swelling-shrinkage behaviour, which suggests that a high content of montmorillonite, can slow down organic matter decomposition by absorption, interacting with soil microbes and their external enzyme activity or limiting oxygen diffusion (Vogel et al. 2015). In addition, a recent highly reliable model on SOC on the region the Haploxerert in the present study came from confirmed that these kind of soil (along with other vertisols) have a high ability to stabilize the soil organic matter (Schillaci et al, 2017; Saia et al. 2017). CO_2 and N_2O fluxes reached a peak in the within the first week of incubation, and were higher in the Cambisol than in the Haploxerert. The transient effects of the CO_2 and N_2O emission rates were likely to have resulted from increased gas diffusivity due to the soil disturbance in the establishment of the experiment and the rapid decomposition of the highly-labile free organic fraction (either added or not) (Magid et al. 1999; Baggs et al. 2006). Crop residue distribution within the soil, as reported by several authors (Curtin et al. 1998; Jacinthe et al. 2002; Lian et al. 2016) stimulated and increased CO_2 emissions but with different magnitudes in the two soils. In particular, the difference in CO_2 emissions between soils was reduced when an organic residue (either faba bean or wheat) was added. The Cambisol emitted +88% and +152% more CO_2 than the Haploxerert when faba bean and wheat residues were added, respectively. Similar differences were found for N_2O emission between soils amended with organic residues. These findings are supported by research by An et al. (2015) where straw C input to the soil was more effective at stimulating microbial activity and extractable organic carbon in a low fertility soil, than in a high fertility soil, probably as a consequence of the starvation of the soil microbial community (Bastida et al. 2013) and also a possible effect of clay which increases the contact between the substrate and microorganisms. However, their experiment used a soil with a lower clay content (24.9%), and we expect that in the soil used in our study which was more rich in clay (52.5%), this effect was less important due to the absorption effects described above. Other studies have shown that an increasing clay content (achieved by making artificial soils) accelerated the decomposition rate of added organic matter supporting the concept that clay can have a primary role in influencing decomposition-stabilization processes in the soil regulating the nutrient availably for microorganisms, emissions and organic carbon stabilization and sequestration (Velthof et al. 2002; Six and Paustian 2014; Wei et al. 2014; Bajgai et al. 2014). Nitrous oxide emissions from the Haploxerert were affected also by soil clay content and it's direct action on N immobilization processes, as observed also by Begum et al. (2014) in an experiment conducted in a same type of soil (Vertisol) with a comparable clay content (62%), closely linked to the stabilization of the organic matter and confirmed by the high NH_4^+-N:NO_3^--N observed. Furthermore, as result of the

the high cation exchangeable capacity of this soil (35 cmol kg^{-1}) the addition of organic matter had a no effect on the pH, whilst in the Cambisol the wheat straw significantly reduced pH, most probably as a consequence of the nitrification process which may acidify soil due to the release of H^+ ions (Van Miegroet and Cole 1983). This would have been promoted by the high degradability of wheat residues, that produced a higher nitrate content in the soil and promoted gaseous emissions (both CO_2 and N_2O) compared to the soil where faba bean was added. In another experiment Aye et al. (2016) using wheat and field-pea, with a different C:N ratio, as residues in a soil with 29% clay found an increase in the decomposition process up to pH 7.4. However, in our experiment, although the pH of the Haploxerert was slightly higher (7.8), the lower DOC concentration, CO_2 and N_2O fluxes in Haploxerert, suggest that the lower decomposition rates that can be linked to the much higher clay content (52.5%) confirming the dominant influence of clay as key factor in determining nutrient turnover and emissions in this soil. The original pH of the soil may have played a role in determining the magnitude of N_2O emissions by the soil microbial community. As reported from Rousk et al. (2009), an acid pH at around 6 can stimulate fungal growth; fungi are recognized for not having the ability to synthesise nitrous oxide reductase and their denitrification end product is therefore N_2O. Other studies have reported that fungi could contribute up to 18% of potential denitrification (Herold et al. 2012). Thus pH differences may also have contributed to differences in N_2O emissions from soils.

There was a clear correlation between CO_2 and N_2O emissions in both soils, although this was greater in the Cambisol, where oxygen depletion and CO_2 emissions could have helped create anaerobic microsites in the soil increasing denitrification and N_2O production (Gök and Ottow 1988; Aulakh et al. 1991; Begum et al. 2014; Nett et al. 2015). The mineralization rate of an organic residue added to the soil mostly depends on its C:N ratio and to a lesser extent to its lignin:N ratio and fibre content (Trinsoutrot et al. 2000; Nguyen and Marschner 2016; Cheng et al. 2015). However, in the present study, the difference in the C:N ratio of the residues used (38.6 in faba bean and 40.7 in wheat) does not explain the difference in soil mineral N concentration and CO_2 and N_2O emissions between the crop residues. Thus, it is more likely that mineralization rate of faba bean residues was lower than wheat residues due to the different lignin, acid detergent, and neutral detergent fibre contents (+188%, +66%, +19%, respectively in faba bean comparing to wheat).

The incorporation of plant residues, either of wheat or faba bean, introduced contrasting effects on the NH_4^+-N and NO_3^--N concentrations on each of the soils. The addition of plant residues increased the NH_4^+-N concentration of the Haploxerert, but not that of the Cambisol, and such an increase was more evident when wheat residues were added. At the same time, addition of plant residues reduced the total NO_3^--N content of the Cambisol, but not that of the Haploxerert, and such an effect was more evident when faba bean residues were added. Such a result points to a net immobilization process in the soil due to consumption of N in order to decompose organic C (Corbeels et al. 2000; Jin et al. 2013). In the Haploxerert, a similar quantity of total CO_2 was emitted after the addition of both crop residues, but the faba-bean addition showed a slightly higher N_2O emission than wheat addition treatment coupled with lower NO_3^--N content at the end of the experiment. Thus, it is likely that in this soil, which was characterized by a lower soil microbial activity, the lower mineralization of faba bean residues led to a more constant availability of labile C and N, due stimulating bacterial and fungal activity along the experiment until the end, and as consequence, denitrification in soil microsites as reported from other authors (Deenik 2006; Shah et

al. 2016). By contrast, wheat residues produced a rapid flush in emission in the initial phase of the experiment and shown at the end of the experiment higher NH_4^+-N and NO_3^--N concentration in to the soil suggesting other limitation. This selective activity of microbes induced by the residue composition results in readily available straw C being used more rapidly while more recalcitrant and stable compounds are decomposed more slowly (Majumder and Kuzyakov 2010). In the Cambisol both crop residues showed the same trend in gas emissions, (CO_2 and N_2O), due to a direct effect of residue characteristics on decomposition and N availability. The rapid mineralization of wheat resulted lower DOC and higher NH_4^+-N and NO_3^--N concentrations and a reduction in pH, as described above. In the case of faba bean the higher presence of recalcitrant compounds, in particular lignin, slowed down nutrient release and decreased emissions.

Comparison between gas flux measurement techniques

This study has clearly demonstrated that IRGA and PGA methodologies used to measure CO_2 and N_2O emissions provided data consistent with that measured by GC. The comparison of CO_2 and N_2O emission rates measured by IRGA and PGA was very strong correlated with GC measurements, an observation also reported by other authors (Pumpanen et al. 2004; Iqbal et al. 2013; Nicoloso et al. 2013; Tirol-Padre et al. 2014). In particular, the same trend was observed for both gas fluxes measured in the Cambisol and Haploxerert, which were characterized by different patterns of CO_2 and N_2O emissions. Similar results to those observed in the present experiment were found for N_2O fluxes by Iqbal et al. (2013), who reported a slightly higher emissions with PGA than with GC (+5%), However, by contrast, we didn't find any difference in CO_2 flux measurements when comparing PGA and GC. Nicoloso et al. (2013) observed an overestimation of 18.6% and 13.6% comparing PGA to GC, for CO_2 and N_2O respectively; we did not find any differences between the techniques, which may have been due to the lower gas concentrations measured during our experiment. That also defined, the positive effect of the compensation against water vapor and cross interference, the two main sources of interference on measurement, during the experiments.

With regard to the accuracy of CO_2 emission data recorded by IRGA, if comparing our performance with those obtained from Pumpanen et al. (2004), the latter of which are based on CO_2 concentration measurements, we obtained better results with very similar fluxes between IRGA and GC. The quality of data obtained from EGM-4 IRGA used in the present study was also confirmed by Mills et al. (2011) who found good similarity in soil respiration flux with a different IRGA type. However, PGA was found to have some limitations in reporting CO_2 fluxes measured by IRGA in the first part of the experiment and monitoring the emissions of Haploxerert control in the later part of the experiment, showing some difficult on measure low and high peak of emission producing a slight overestimation on data. At medium and low emission rates the instruments performances were similar and this was also confirmed by GC. Taking into account the reliability of data, together with the speed of measurement, and the capacity to obtain high resolution temporal data, this study highlights the benefits of using online IRGA and PGA measurements in studies of residue decomposition. When applied in the field experiment, the short time required from IRGA and PGA to take a measurement of emission provides an opportunity to make more measurements permitting a higher spatial and temporal resolution. In the case of the PGA, the results produced had a

considerable importance due to the possibility of this instrument to measure two or more gaseous compounds simultaneously Horsley et al. 2014.

Finally, although the chamber techniques coupled with GC is considered the reference technique for the GHG monitoring, direct measurement by these devices eliminates many of the risks resulting from sampling pitfalls and sample storage that can negatively affect the measurements (Cowan et al. 2014; Tirol-Padre et al. 2014). For the specific application to GHG studies, the initial cost and maintenance can be lower than GC systems, requiring also less specialized staff to operate. The comparison of CO_2 emissions rates measured by IRGA and PGA across the entire experimental period revealed, overall, that there were small differences between both methods.

Conclusions

Soil plays a major role in controlling GHG emissions to the atmosphere and are a key determinant of emissions originating from plant residues. Our study demonstrated, when comparing two different soils, how specific proprieties, such as clay content and pH, can significantly alter decomposition, immobilization and gaseous emissions. These results have implications for developing low-C management practices, especially under organic farming systems where residue management could be a strategy to replace mineral fertilizers and limit C footprint. In Vertisols, which are widespread, but less well understood, CO_2 and N_2O emissions were strongly controlled by clay content limiting emissions, promoting C sequestration and N transfer to next crop cycle. Although many studies on the decomposition of residues have focused on C/N ratios, this study highlights the importance of fibre compounds, often referred to as secondary, on determining soil CO_2 and N_2O emissions and as their effect can change in relation to the soil characteristics. In particular, in soil with high organic carbon contents and microbial activity such as a Cambisol, the crop residue type determined the total emission. There was a unique trend for higher emissions of both gases (CO_2 and N_2O) in the presence of more decomposable wheat than with recalcitrant faba bean. In Haploxerert, by contrast, the slower decomposition of crop residues resulted in a similar CO_2 release from the different residues, but slightly higher N_2O emissions from faba bean.

The direct comparison between IRGA and PGA and their validation with GC confirmed that these two techniques are equivalent in providing reliable data for long-term monitoring, and this occurred under various conditions (differing soil type residue addition). This result is important when considering that GC-based methodologies need of a number of sample steps from gas collection, transport, sample storage, and analysis, each of which can potentially add error to the measurement. In addition, GC-based methodologies are not able to provide a continuous measurement of the GHG emissions and thus are poor at quantifying temporal variability. By contrast, the high sensitivity of IRGA and PGA, range and ease of application, number of gases analyzed (including water vapor) allow a better monitoring of the radiative force of the soil while eliminating many of the risks of the GC-based methodologies.

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Tables and Figures

Table 1 Main properties of soils.

Soil Properties	Scotland Bush Estate	Sicily Pietranera
Soil classification	Eutric Cambisol	Chromic Haploxerert (Vertisol)
Soil series	Macmerry	Gessoso-solfifera (sulphurous-chalky)
Texture	Sandy-loam	Clay-loam
Coordinates	55.9 N, 3.2 W	37.3 N, 13.3 W
Altitude	199	178
Slope [%]	6	7
Clay [%]	12.7	52.5
Silt [%]	15.7	21.6
Sand [%]	71.6	25.9
pH	6.6	8.1
Field capacity (pF 2.5) [%]	36	38
Permanent wilting point (pF 4.5) [%]	20	16
Organic matter [%]	4.3	2.4
Total N [%]	0.21	0.13

774 **Table 2** Composition of crop residues.

Chemical properties of crop residues	Faba Bean	Durum Wheat
Organic Matter	91.8	92.1
N content	1.4	1.3
Crude protein	8.8	8.1
Ether extract	1.1	1.7
Acid detergent fibre (ADF)	48.0	28.8
Acid detergent lignin (ADL)	10.0	3.5
Cellulose	38	25.3
Neutral detergent fibre (NDF)	54.0	45.4
Hemicellulose	6	16.6
Ash	8.2	7.9
ADL Ash	0.4	3.2

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Table 3 Effect of the addition of two crop residues (Durum wheat or fababean, and unamended control) on Dissolved Organic C (DOC), pH, NH_4^+-N and NO_3^--N content and NH_4^+-N: NO_3^--N ratios in 0-5 cm and 5-15 cm soil layers of a Chromic Haploxerert and Eutric Cambisol soils.

		Chromic Haploxerert			Eutric Cambisol			*P*		
		Faba bean	Durum wheat	No addition	Faba bean	Durum wheat	No addition	*Soil*	*Residue Type*	*S × T*
0-5 cm soil layer										
DOC	mg C kg^{-1} soil	42.5	43.2	33.6	73.5	67.6	67.2	*<.001*	*0.000*	*0.007*
pH	-	7.7	7.8	7.8	5.8	5.4	5.9	*<.001*	*0.009*	*0.019*
NH_4^+-N	mg N kg^{-1} soil	1.6	3.3	1.7	0.9	1.3	0.9	*<.001*	*<.001*	*<.001*
NO_3^--N	mg N kg^{-1} soil	0.4	2.4	0.3	104.6	149.6	164.5	*<.001*	*0.001*	*0.001*
NH_4^+-N: NO_3^--N	-	4.3	1.4	6.5	0.009	0.008	0.006	*<.001*	*0.001*	*0.001*
5-15 cm soil layer										
DOC	mg C kg^{-1} soil	75.9	83.0	48.1	86.4	93.1	91.8	*<.001*	*<.001*	*<.001*
pH	-	7.7	7.7	7.8	5.9	5.6	5.8	*<.001*	*0.037*	*0.043*
NH_4^+-N	mg N kg^{-1} soil	13.5	32.0	5.8	1.1	1.5	0.9	*<.001*	*<.001*	*<.001*
NO_3^--N	mg N kg^{-1} soil	0.5	0.5	0.8	36.9	43.3	66.4	*<.001*	*<.001*	*<.001*
NH_4^+-N: NO_3^--N	-	25.7	62.9	7.3	0.030	0.034	0.014	*<.001*	*<.001*	*<.001*

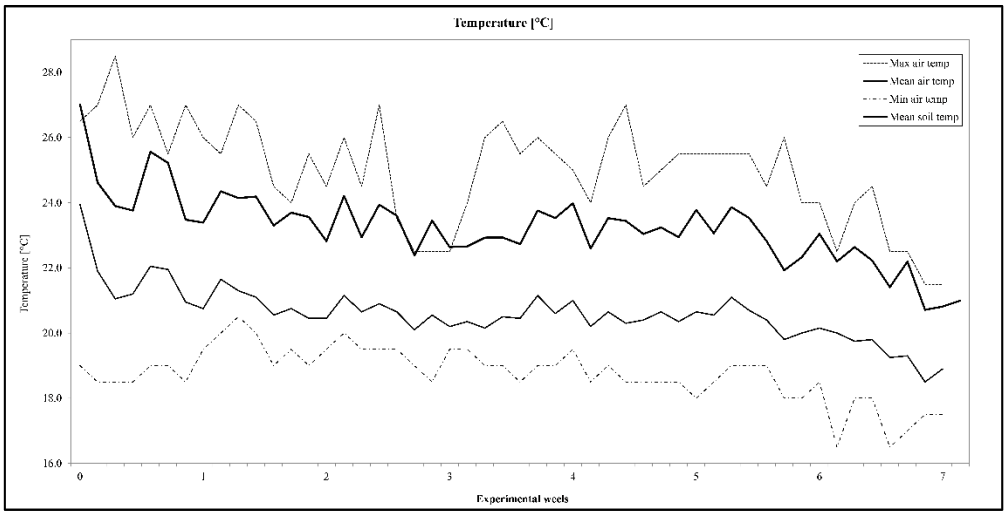

Fig. 1 Daily minimum, maximum, mean air temperature in the greenhouse and mean soil temperaure during the experiment

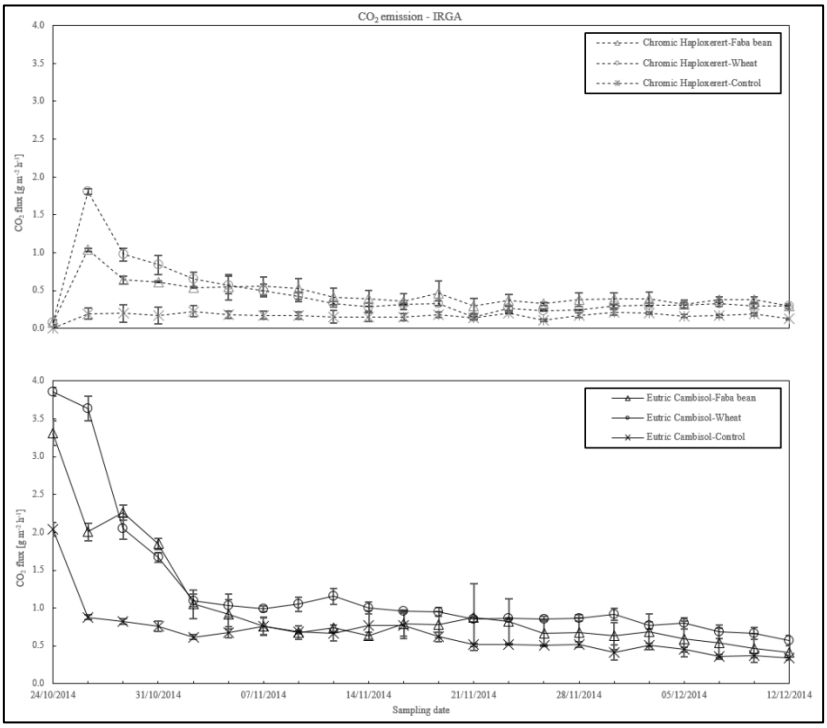

Fig. 2 CO_2 emission course from Chromic Haploxerert and Eutric Cambisol amended with faba bean and wheat residues, or unamended (control), measured with IRGA during the experimental period. Data are means±S.E (n=3)

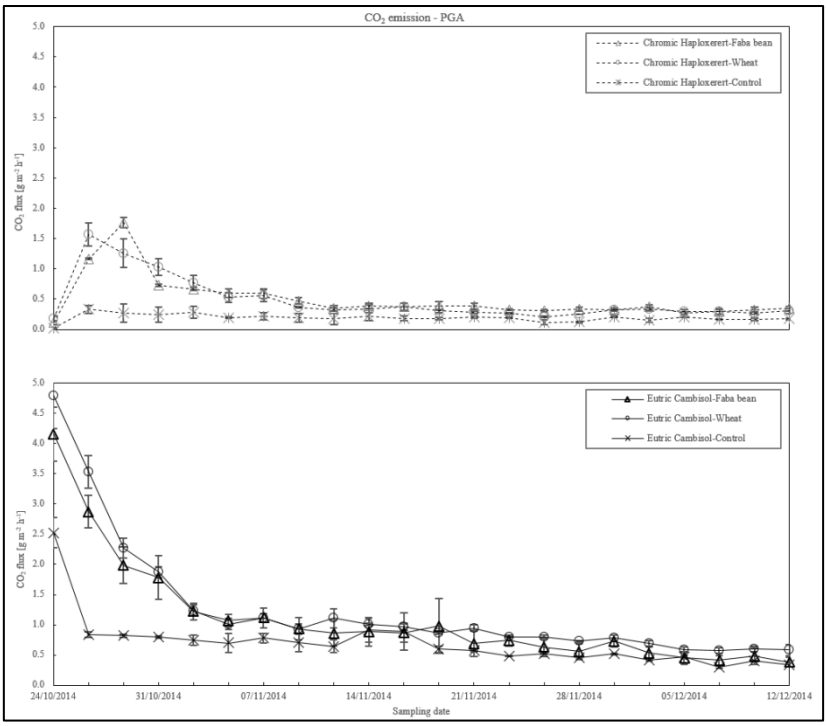

Fig. 3 CO_2 emission course from the Chromic Haploxerert and Eutric Cambisol soils amended with faba bean and wheat biomass, or unamended (control), measured with PGA during the experimental period. Data are means±S.E (n=3)

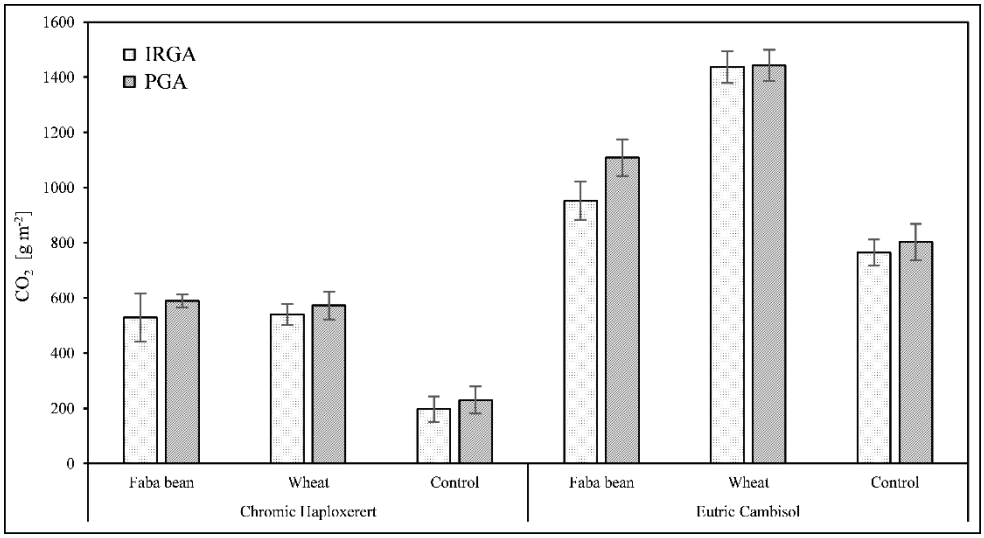

Fig. 4 Total CO_2 emission from the Chromic Haploxerert and Eutric Cambisol amended with faba bean and wheat biomass, or unamended (control), measured with IRGA and PGA. Data are means±S.E (n=3)

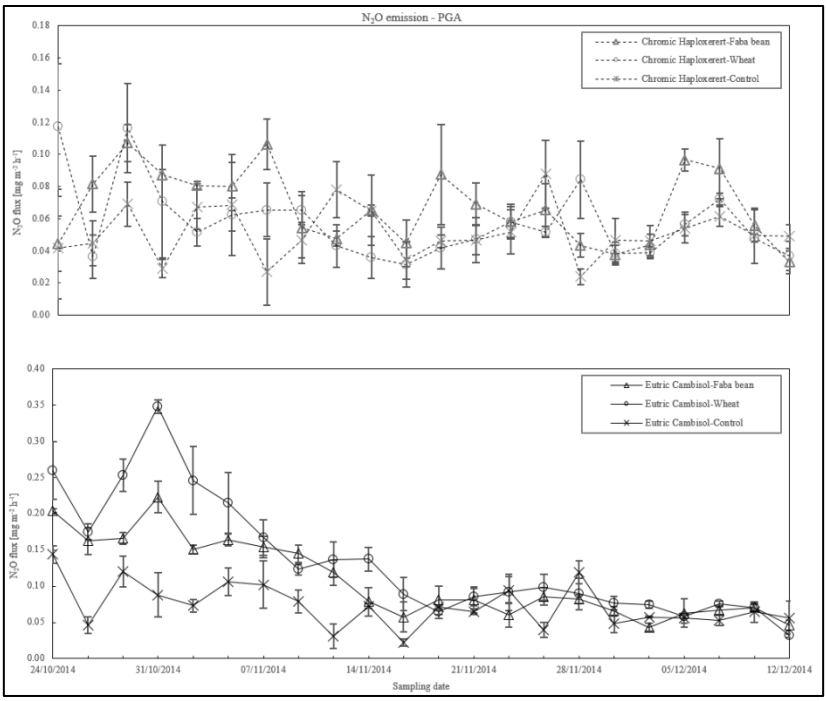

Fig. 5 N_2O emission course from the Chromic Haploxerert and Eutric Cambisol amended with faba bean and wheat biomass, or unamended (control), measured with PGA during the experimental period. Data are means±S.E (n=3)

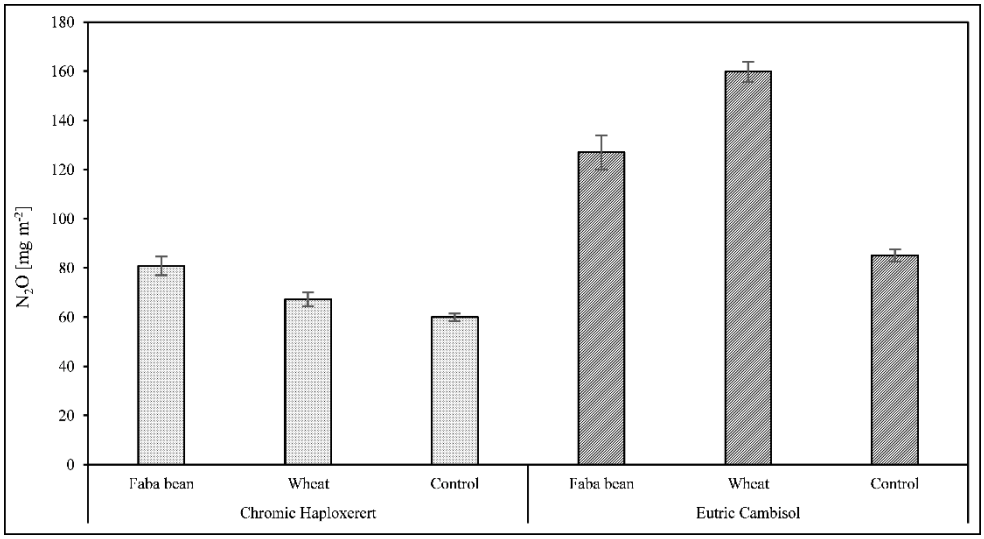

Fig. 6 Total N_2O emission from the Chromic Haploxerert and Eutric Cambisol soils amended with faba bean and wheat biomass, or unamended (control), measured with PGA. Data are means±S.E (n=3)